6-1-1969

The reaction products and the kinetics of the reactions between hypochlorite ions and thiosulfate and tetrathionate ions

Thomas Dagon

THE REACTION PRODUCTS AND THE KINETICS OF THE REACTIONS BETWEEN HYPOCHLORITE IONS AND THIOSULFATE AND TETRATHIONATE IONS

THOMAS J. DAGON

JUNE, 1969

SPECIAL REPORT

SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

John A. White
Project Adviser

R. L. Craven
Department Head

T. E. Strader
Library

Rochester Institute of Technology
Rochester, New York

ABSTRACT

The reaction products of the hypochlorite oxidation of both thiosulfate and tetrathionate solutions were determined. In addition, preliminary kinetic studies were made dealing with the alkaline chlorination of thiosulfate solutions and with the hypochlorination of tetrathionate solutions. In the latter case, a pH dependent induction period was observed.

INTRODUCTION

The purpose of this research is to investigate the mechanism of the oxidation of thiosulfate and tetrathionate with hypochlorite and to study the kinetics of these reactions.

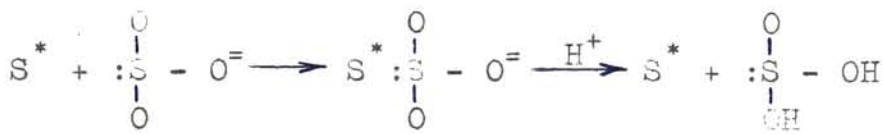
The thiosulfate ion is an oxy-compound of sulfur in which the sulfur is present in an intermediate oxidation state, positive two. The most common of the thiosulfates is sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), commonly, but incorrectly, referred to as hypo. The thiosulfate ion is relatively staole in a neutral or alkaline media. However, neither free thiosulfuric acid nor hydrogen thiosulfate salts can be readily prepared because of reactions between thiosulfate and hydrogen ions. However, the free acid has been isolated as an etherate[1] at -78 C from the following reaction:

$$SO_3 + H_2S \longrightarrow H_2S_2O_3$$

The decomposition reactions depend on the hydrogen ion concentration. At hydrogen ion concentrations below pH 4.6, the $HS_2O_3^-$ ion could be formed, but would undergo immediate decomposition to sulfur and sulfur dioxide. The lower the pH, the more rapid is the decomposition. It has been reported[2] that some pentathionate is slowly formed at the same time. Under some conditions, when concentrated hydrochloric acid is added to thiosulfate,

hydrogen sulfide and persulfide are also formed in small amounts.

The thiosulfate ion is a structural analog of the sulfate ion in which a sulfur atom has replaced one oxygen atom in the sulfate. This structure is compatible with the observation that if thiosulfate, synthesized using ordinary sulfite and radioactive elemental sulfur, is acidified, almost all of the radioactivity is precipitated with the elemental sulfur which is regenerated.[3,4] This shows that the sulfur atoms in the thiosulfate are not equivalent. This is shown below:



The thiosulfate ion is a moderately strong reducing agent. The most common oxidation reaction it undergoes is the conversion of the thiosulfate to tetrathionate by iodine.

$$2S_2O_3^{=} + I_2 \longrightarrow 2I^- + S_4O_6^{=}$$

This reaction is widely used in the volumetric determination of iodine. Most often, a neutral or slightly acidic solution of iodine in potassium iodide is titrated with thiosulfate. Then the following reaction occurs rapidly and stoichiometrically.

$$I_3^- + 2S_2O_3^{=} \longrightarrow 3I^- + S_4O_6^{=}$$

While mixing is rapid and some tetrathionate is formed

immediately, it has been shown[5] that an intermediate $S_2O_3I^-$ is formed by a fast, reversible reaction.

$$S_2O_3^{=} + I_3^- \rightleftharpoons S_2O_3I^- + 2I^-$$

This intermediate reacts with iodide.

$$2S_2O_3I^- + I^- \longrightarrow S_4O_6^{=} + I_3^-$$

This accounts for the reappearance of iodine near the end point in the titration of very dilute iodine solutions. The intermediate also reacts with the thiosulfate, providing the main portion of the overall reaction.

$$S_2O_3I^- + S_2O_3^{=} \longrightarrow S_4O_6^{=} + I^-$$

It has been found that the rate law for the formation of tetrathionate involves the second power of the $S_2O_3I^-$ ion concentration. Although this reaction is generally stoichiometric, several complications can occur. First, at low concentrations of iodide (0.003 M) the stoichiometry is no longer exact, because of some sulfate formed by the reaction:

$$S_2O_3I^- + 3I_3^- + 5H_2O \longrightarrow 2SO_4^{=} + 10H^+ + 10I^-$$

Also, tetrathionate will undergo slow oxidation by excess iodine to form sulfate[6], but the reaction is too slow to be important under the usual analytical conditions.

As long as the pH is kept below 5, the iodine-thiosulfate reaction is accurate. However, in alkaline solution, (pH = 8), iodine will react to form hypoiodite ion[7]

$$I_2 + 2OH^- \rightleftharpoons OI^- + I^- + H_2O$$

The hypoiodite ion should then partially oxidize the thio-

sulfate to sulfate.[8] This would affect the titration of iodine with thiosulfate. However, the effect on the reverse reaction would be small because the rapid thiosulfate reaction would consume the iodine before it could react with the hydroxyl ion. In a very strong alkaline solution, the reaction will go quantitatively to sulfate.[9]

It was expected that the chlorine (or hypochlorite) oxidation of thiosulfate would be similar to that of the iodine oxidation. In fact, it has been noted[10] that thiosulfates are oxidized to tetrathionates by mild oxidizing agents such as Fe^{+3}, Cu^{+2}, PbO_2, Na_2O_2 and SeO_2. One such reaction is shown by the following equation:

$$2Na_2S_2O_3 + 2FeCl_3 \longrightarrow 2NaCl + 2FeCl_2 + Na_2S_4O_6$$

Since chlorine is a stronger oxidant, it would be expected that the reaction would yield mainly sulfate. Lunge[13] said that the chlorination of a sodium thiosulfate solution resulted in the following reaction:

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

He also pointed out that some tetrathionate was probably produced. Another source[14] states that the chlorination of thiosulfate results in the formation of sulfate and polythionates. Later, it was determined that the hypochlorination of a dilute thiosulfate solution resulted in the following reaction:

$$3Na_2S_2O_3 + 5NaOCl \longrightarrow 2Na_2SO_4 + Na_2S_4O_6 + 5NaCl$$

A more vigorous reaction would result in the complete

conversion of tetrathionate to sulfate. Glasstone and Hickling[15] found that tetrathionate was formed when thiosulfate was electrolyzed in the presence of H_2O_2. Finally in a 1935 article[16] pertaining to an analytical method for determining available chlorine in a hypochlorite solution, Willson claimed that the hypochlorination of a thiosulfate solution followed one of the three following reactions, depending on the molecular ratios of the reacting substances.

$$2Na_2S_2O_3 + NaClO + H_2O \longrightarrow Na_2S_4O_6 + 2NaOH + NaCl$$

$$Na_2S_2O_3 + 4NaClO + H_2O \longrightarrow 4NaCl + Na_2SO_4 + H_2SO_4$$

$$3Na_2S_2O_3 + 5NaClO \longrightarrow Na_2S_4O_6 + 5NaCl + 2Na_2SO_4$$

In this and all the other cases, no mention was made as to the exact nature of another polythionate formed as an intermediate in the oxidation of thiosulfate. This could have been due to the lack of rigorous analytical methods for determining the polythionates at the time the various experiments were carried out. Under the various possible conditions involved in the chlorination (or hypochlorination) of thiosulfate, there is certainly a possibility of these species existing even, with the exception of the tetrathionate, if only in small amounts and even if they result from a secondary reaction rather than from the direct chlorination.

The polythionates have the general formula $(O_3S\ S_n\ SO_3)^{-2}$. The most common ones are those where n is

equal to from 1 to 4. These include the trithionate, $S_3O_6^=$, the tetrathionate, $S_4O_6^=$, the pentathionate, $S_5O_6^=$, and the hexathionate, $S_6O_6^=$. It has been definitely established for all four of these species that there are sulfur chains.[17] This has disproven previous proposals commonly found in older articles that there might be S → S linkages.[18] Dithionate is generally not considered a polythionate. As with thiosulfate, the free acids are not stable. They decompose rapidly into sulfur, sulfur dioxide, and sometimes sulfate depending upon the conditions. However, the salts are fairly stable under certain other conditions. The production of polythionates from thiosulfate, in addition to tetrathionate, has been noted. Trithionates have been found after the treatment of thiosulfates with SO_2 and also treatment with H_2O_2.[19] This reaction is given as:

$$2Na_2S_2O_3 + H_2O_2 \longrightarrow 2NaOH + Na_2S_4O_6$$

$$\xrightarrow{-S} Na_2S_3O_6 + Na_2SO_4 + H_2O$$

The formation of hexathionate was noted when thiosulfate was treated with KNO_2 in cooled hydrochloric acid.[20] Another source states that prolonged treatment of thiosulfate with sulfur dioxide resulted in the production of tri, tetra, and pentathionates.[21] Another earlier article[22] relates that the treatment of thiosulfate with hydrogen peroxide in an alkaline solution resulted in the formation

of some dithionate, according to the reaction:

$$4Na_2S_2O_3 + 8H_2O_2 \xrightarrow{OH^-} 2Na_2SO_4 + Na_2S_2O_6 + Na_2S_4O_6 + 8H_2O$$

Thus, all the polythionates and also dithionate can result from thiosulfate. Part of the objectives of this study is to determine whether or not any of these substances are formed during the chlorination of a thiosulfate solution.

There are several possible approaches to the "chlorination" of a solution. First, chlorine gas could be bubbled into the thiosulfate or tetrathionate solution. The efficiency of this reaction is poor and unless the system is buffered, the system will become acidic. A second approach would be to saturate water with chlorine, and then react the chlorine water with the solution. Chlorine will dissolve. However, species other than the solvated chlorine will be present, since a rapid disproportionation occurs. Two equilibria result.

1.) $Cl_2(g) \rightleftharpoons Cl_2(aq)$ $\quad K_1 = 6.2 \times 10^{-2}$

2.) $Cl_2(aq) \rightleftharpoons H^+ + Cl^- + HOCl$ $\quad K_2 = 4.2 \times 10^{-4}$

Thus at 25 C, the total solubility of chlorine in water is 0.091 M. The $Cl_2(aq)$ concentration will be 0.061 M and the HOCl concentration will be 0.030 M. Thus two different oxidizing agents will actually be present in such a solution.[23] An additional complication can occur due to the disproportionation of the hypochlorite ion according to the reaction:

$$3ClO^- \longrightarrow 2Cl^- + ClO_3^-$$

Thus a weaker oxidizing agent, the chlorate ion might be present. This disproportionation is slow at room temperature, but is rapid at high temperatures, such as 75 C.

A third method of "chlorinating" the thiosulfate would be to bubble chlorine into the solution and at the same time add sodium hydroxide, keeping the pH 11. Hypochlorite would be readily formed and would act as the oxidizing agent. The continuous addition of hydroxide would in effect buffer the solution.

Finally, a solution of hypochlorite could be reacted with the thiosulfate or tetrathionate solution. If allowed to proceed in an unbuffered system, the pH would eventually drop well below 7. Due to the nature of the starting material, and the possible intermediate products, the pH of the system could determine which materials would be formed in the reactions.

It was decided that the "chlorination" would be carried out using sodium hypochlorite. The "chlorination" would be carried out so that the oxidation proceeded about half way to completion. Complete oxidation in any case would result in the production of sulfate only and no polythionate. This work is described in the experimental section.

After the products of the various reactions have been determined, the kinetics of the reactions are studied.

EXPERIMENTAL

A. Determination of Reaction Products

The first part of this work was planned to determine the products resulting from the partial oxidation of thiosulfate and tetrathionate by hypochlorite.

Preliminary work established the existance of an intermediate form in the chlorination of thiosulfate. Two liters of 0.36 M thiosulfate solution were chlorinated for 75 minutes at a flow rate of one liter of chlorine per minute. The apparatus used is shown in Figure 1 on the following page. Ten M NaOH was added continuously during the chlorination so that the chlorine would be converted to hypochlorite. The solution was sampled at various time intervals and analyzed for thiosulfate[24] and chemical oxygen demand.[25] The chemical oxygen demand test essentially measures oxidizable material which is present. A known volume of sample is refluxed with an acid dichromate mixture and the dichromate reduction is measured. Whereas the thiosulfate concentration was reduced to zero in thirty five minutes, there was still an appreciable chemical oxygen demand. Since the chemical oxygen demand was measured using an automated Technicon method in which chloride ion did not contribute to the oxygen demand, the only other possibility was that an intermediate compound of sulfur was being formed and the further oxidized.

Figure 1

CHLORINE APPARATUS

In order to verify that an intermediate form was present, samples were taken after 45, 60 and 75 minutes of chlorination. The samples were analyzed for chloride content and sufficient silver nitrate solution was added to each solution to provide a slight excess after the precipitation of all silver chloride. If any thiosulfate or polythionate were present, a reaction of the type shown below occurs resulting in a dark precipitate.

$$2AgNO_3 + Na_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4 + 2NaNO_3$$

If no thiosulfate of polythionates were present, only the white silver chloride precipitate would result. When the 45 and 60 minute samples were treated, dark precipitates resulted. However, a white precipitate resulted when the 75 minute sample was treated indicating that only sulfate remained. Chemical oxygen demand measurements on the 75 minute solution after chloride removal verified that all of the oxidizable material was gone. Chemical oxygen demand measurements could not be made on samples having low chemical oxygen demands and high chloride contents because of the formation of silver chloride precipitate in the analyzer lines. This results from the reaction between chloride ion and silver ion present as a catalyst in the method. Thus an intermediate species must result from the chlorination of thiosulfate solution.

Further reactions were carried out in a liter beaker.

First, 500 milliliters of a 0.20 M thiosulfate solution, Solution A, was placed in the container. Next 37.5 milliliters of 2 M sodium hypochlorite solution was added to the beaker while the solution was being constantly stirred. The temperature was monitored throughout the reaction. pH was also monitored throughout the reaction. The amount of sodium hypochlorite solution was chosen to carry the reaction approximately one-half to completion. The solution was stirred for one-half hour. The solution was then analyzed for thiosulfate, sulfite, trithionate, tetrathionate, pentathionate, and hexathionate using the method of Kurtenacher and Goldbach.[24] This method is described in Appendix I.

Three other experiments were carried out involving variation of the pH. Experimental conditions were identical with the exception of the pH and the volume of hypochlorite added. In the first case, Solution B, the reaction was allowed to proceed and the pH was adjusted to 7.1 with 3 milliliters of 7 M sulfuric acid. In the second case, Solution C, 40 milliliters of 2 M sodium hypochlorite and 5 milliliters of 10 M sodium hydroxide was added to the solution. The caustic in effect buffered the solution at pH 12. This is the pH at which alkaline chlorination would be carried out. Next 50 milliliters of 2 M sodium hypochlorite solution was added to the solution and 4 milliliters of 7 M sulfuric acid was added to

adjust the pH to 4.6. This solution is labeled as Solution D.

A 0.40 M thiosulfate solution was prepared. 500 milliliters of this solution was placed in a one liter beaker. 100 milliliters of 2 M sodium hypochlorite was then added to the thiosulfate solution. This mixture was sampled and analyzed after thirty minutes, (Solution E), and again after four hours, (Solution F). This was done to evaluate how well the reactant and products were equilibrated among themselves. Several milliliters of sulfuric acid was added to adjust the pH to 7.1.

Two tests were carried out to determine the products resulting from the hypochlorination of a tetrathionate solution. First, 250 milliliters of a 0.44 M tetrathionate solution was mixed with 7 milliliters of 2 M sodium hypochlorite solution, (Solution G). Finally, 250 milliliters of the same tetrathionate solution was reacted with 10 milliliters of 2 M sodium hypochlorite and the pH was adjusted to 7 with several milliliters of sulfuric acid. This solution is labeled as Solution H.

In all the above cases, the solutions were analyzed as mentioned previously. All results are given in the next section.

B. The Kinetics of the Oxidation of the Thiosulfate Ion and the Tetrathionate Ion by the Hypochlorite Ion.

Some preliminary work was carried out to investigate

the kinetics of the thiosulfate oxidation. This work was carried out using the equipment shown previously in Figure I. Chlorine was bubbled into the solution at a constant rate and the pH was held constant at pH 11.5 by the addition of 10 M sodium hydroxide. Thus the hydroxide ion concentration was in excess and was not expected to affect the rate of the following reaction:

$$S_2O_3^{=} + 4Cl_2 + 10\ OH^- \longrightarrow 2SO_4^{=} + 5H_2O + 8Cl^-$$

Three reactions were carried out with thiosulfate concentrations of 0.181 M (Solution I), 0.363 M (Solution S), and 0.725 M (Solution N). The chlorine flow rate for these experiments were held constant at one liter of chlorine per minute. Two more experiments were carried out using 0.363 M thiosulfate solution and chlorine flow rates of 0.5 (Solution L) and 1.5 (Solution M) liters per minute. The results of these experiments are given in the following section.

The limitations of this kinetic study were recognized and a more thorough study was undertaken. It was decided to study the kinetics of the reaction between tetrathionate and hypochlorite. The expected reaction is:

$$7ClO^- + S_4O_6^{=} + 6OH^- \longrightarrow 4SO_4^{=} + 7Cl^- + 3H_2O$$

The study was done spectrophotometrically. It was known that the hypochlorite ion has a peak absorption near 300 millimicrons.[26] If none of the other species which might be present in solution absorb at this wavelength, the

reaction rate could be monitored by mixing the tetrathionate and hypochlorite and following the absorption with time. Absorption curves were run on the solutions shown below between 250 and 350 millimicrons.

NaClO solution	$Na_2S_2O_3$ solution
Na_2SO_4 solution	NaCl solution
$Na_2S_4O_6$ solution	Na_2SO_3 solution

The curves for the tetrathionate and hypochlorite solutions are shown in Figures 2 and 3. Above 300 millimicrons, only these absorb and consequently only these two absorbtion curves are shown. The tetrathionate absorption is fairly significant at 300 millimicrons, however at 320 millimicrons, the absorption is minimal at the planned experimental concentration while the hypochlorite still has a significant absorption. At this wavelength the ratio of the absorbance of hypochlorite to the absorbance of tetrathionate was the maximum. Consequently, it was determined that the kinetics could be studied by following the absorption at 320 millimicrons.

The experiments were carried out so that the following concentrations of chemicals were reacted.

a) 2 mm/l NaClO + 2 mm/l $Na_2S_4O_6$

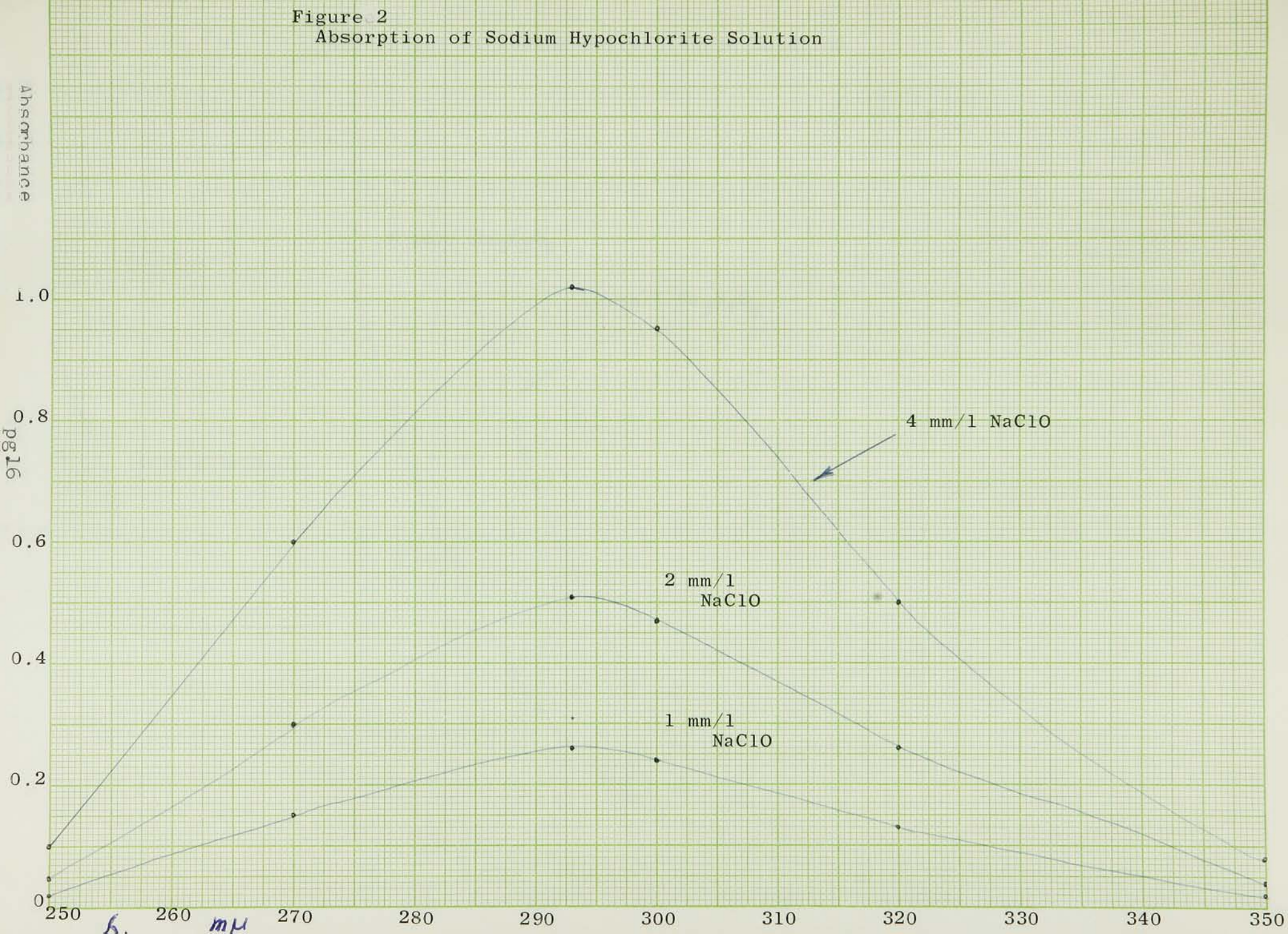
b) 2 mm/l NaClO + 1 mm/l $Na_2S_4O_6$

c) 2 mm/l NaClO + 0.5 mm/l $Na_2S_4O_6$

d) 4 mm/l NaClO + 1 mm/l $Na_2S_4O_6$

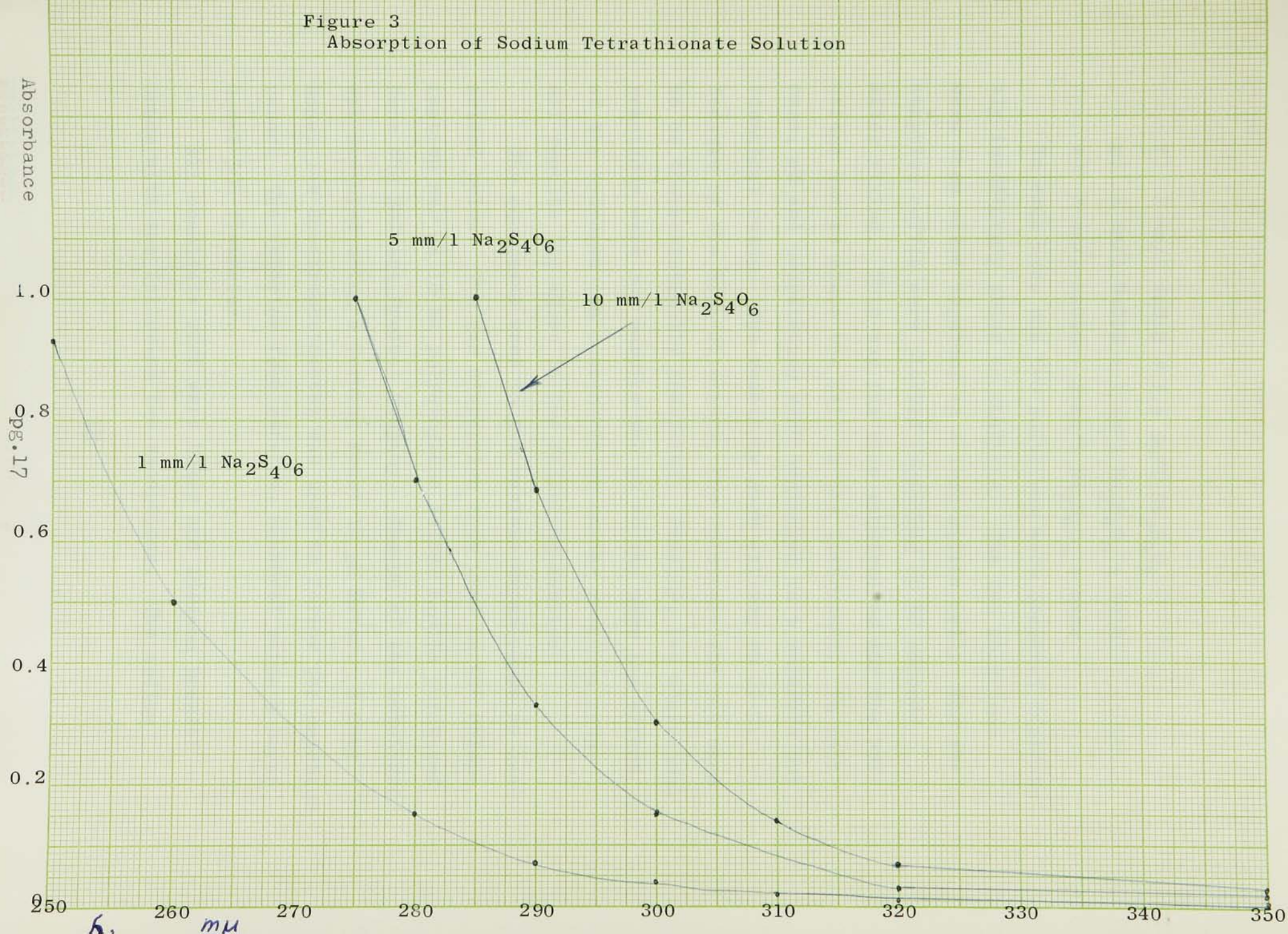
e) 1 mm/l NaClO + 1 mm/l $Na_2S_4O_6$

Figure 2
Absorption of Sodium Hypochlorite Solution



pg16

Figure 3
Absorption of Sodium Tetrathionate Solution



f) 2 mm/l NaClO + 1.5 mm/l $Na_2S_4O_6$

g) 2 mm/l NaClO + 1 mm/l $Na_2S_4O_6$ + acid

h) 2 mm/l NaClO + 1 mm/l $Na_2S_4O_6$ + base

In each case the two solutions were prepared separately immediately prior to analysis. The two solutions were then mixed together in a 1-cm silica cell. The absorption curves were plotted beginning at 30 seconds after mixing. This was the time required to mix the solutions and to place the cell in the instrument. In each case, pH and temperature were monitored in a separate but identical setup. The reactions were all run at 25 C. Because of the high dilutions, the solutions did not need to be thermostatically insulated. Finally, two additional reactions were run varying the pH to the show the effect of the hydrogen ion concentration on the reaction rate. All results are shown in the following section.

The equipment used in the various experiments is described below. The gas dispersion tube used in the chlorination was an 18 mm polyethylene filter candle purchased from the Bel-Art Product Company. The pH of the solutions was measured using a Corning Model 12 pH Meter. A Cary Model 14M Spectrophotometer was used to follow the reaction rates. The chlorine feed rate was measured using a Dwyer Model 500 flowmeter.

All chemicals used were Baker and Adamson Reagent Grade with the following two exceptions. The sodium

hypochlorite solution was a 15% solution of "Sunny Sol." The sodium tetrathionate was prepared by K&K Laboratories, Inc. in Plainview, New York.

RESULTS

A. Determination of Reaction Products

The results of the hypochlorination of the different thiosulfate and tetrathionate solutions are shown in Table I.

It is evident that tetrathionate is indeed formed in the reaction between thiosulfate and hypochlorite. However, it seems that the trithionate ion is also present, possibly either as an intermediate or as the result of a secondary reaction. In fact the trithionate was the predominant species in five of the six experiments. In two of the experiments, analysis showed the presence of pentathionate. The small amounts could have been within the range of the experimental error of the method. However, when the tetrathionate was hypochlorinated, pentathionate was definitely produced. Material balances indicated that sulfate was also formed. No hexathionate was found in any of the solutions.

It is probable that the thiosulfate was oxidized to tetrathionate. The tetrathionate then could have partially decomposed to form free sulfur, which was found in several of the solutions, and trithionate. Pentathionate could result from the partial oxidation of thiosulfate, trithionate, or tetrathionate or from the reaction between either trithionate or tetrathionate and free sulfur.[27]

Table I

RESULTS OF THE HYPOCHLORINATION OF
THIOSULFATE AND TETRATHIONATE SOLUTIONS

Soln.	Orig.* S_2O_3	S_2O_3	SO_3	S_3O_6	S_4O_6	S_5O_6	Temp.	pH	Time**
A	0.20	0.12	0	.037	.012	0	+7 C	8.9	30
B	0.20	0.101	0	.025	.020	.003	---	7.1	30
C	0.20	0.126	0	.024	.004	0	+11 C	12.2	30
D y	0.20	0.074	0	.023	.025	.005	+10 C	4.6	30
E	0.33	0.198	0	.017	.015	.010	+16 C	7.1	30
F	0.33	0.208	0	.019	.016	.003	+16 C	7.0	240
G y	0.44***	0.011	0	.094	.144	.112	+ 4 C	2.7	30
H	0.44***	0.037	0	.056	.153	.088	+ 5 C	7.0	30

* All concentrations in moles per liter.

** All time values in minutes.

*** Values are moles per liter of S_4O_6.

y Some colloidal sulfur was formed during reaction.

Another possibility involves the following reaction:[28]

$$2S_4O_6^{=} \longrightarrow S_3O_6^{=} + S_5O_6^{=}$$

In the hypochlorination of the tetrathionate, a small amount of thiosulfate was found along with trithionate, tetrathionate, and pentathionate. A material balance showed that some of the tetrathionate must have been oxidized to sulfate. The thiosulfate, trithionate, and pentathionate probably resulted from reactions other than the hypochlorite oxidation involving the tetrathionate. In basic solution, tetrathionate is known to decompose to form trithionate.

The results obtained in Solutions E and F show that little reaction occurred after the first one-half hour.

Experimental work also showed that the pH has a great deal of effect on the species present. In one case a 0.64 M thiosulfate solution was mixed with 0.20 M sodium hypochlorite solution. At the end of the reaction, the thiosulfate content had been reduced to about 5 g/l as $Na_2S_2O_3 \cdot 5H_2O$. The pH was approximately 2.8. The pH of the solution was then adjusted to 11.5 with 10 M sodium hydroxide. The solution was again analyzed and the thiosulfate concentration was found to be 55 g/l. The tetrathionate, or any other polythionate present, could have been decomposed in the basic solution to reform thiosulfate as shown by the following reaction.

$$2S_4O_6^{=} + 6OH^{-} \longrightarrow 3S_2O_3^{=} + 2SO_3^{=} + 3H_2O$$

When another 100 milliliters of hypochlorite solution was added to the solution, the pH dropped again to about 3 and analysis showed less than 5 g/l of thiosulfate remaining. Chemical oxygen demand data verified this explanation.

B. The Kinetics of the Oxidation of the Thiosulfate Ion by Chlorine.

The following results were obtained in the experiments dealing with the kinetics of the chlorination of thiosulfate solutions. The thiosulfate concentrations and the chemical oxygen demands were monitored at various time intervals. From the graphs of the thiosulfate and chemical oxygen demand concentrations versus time, shown in Figures 4a, 4b, 5a, and 5b, the initial rates were determined. It was found that halfing or quartering the thiosulfate concentration (original concentration of 180 g/l $Na_2S_2O_3 \cdot 5H_2O$) had no effect on the rate. This could have been due to the thiosulfate being present in such a large excess that concentration changes would have no effect on the rate. When the chemical oxygen demand concentration was plotted versus time on semi-logarithmic paper, Figure 6, a straight line resulted. This is indicative of a first-order reaction. Since the hydroxide was present in excess, as apparently the thiosulfate was, the reaction appeared to be first order in chlorine.

Figure 4a

CHLORINATION OF THIOSULFATE SOLUTIONS (VARYING FLOW RATES)

COD REDUCTIONS

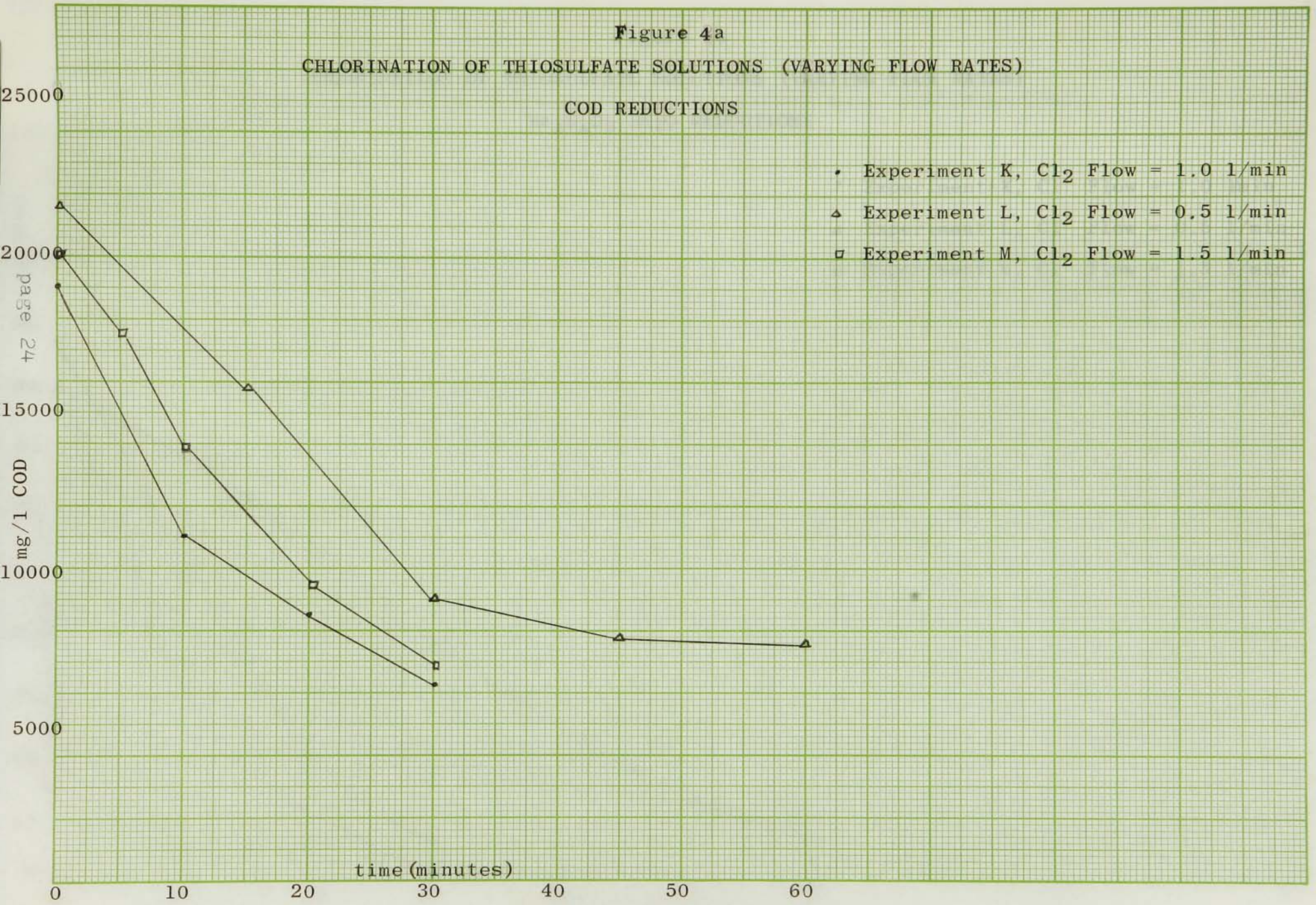


Figure 4b

CHLORINATION OF THIOSULFATE SOLUTIONS (VARYING FLOW RATES)

$Na_2S_2O_3 \cdot 5H_2O$ REDUCTIONS

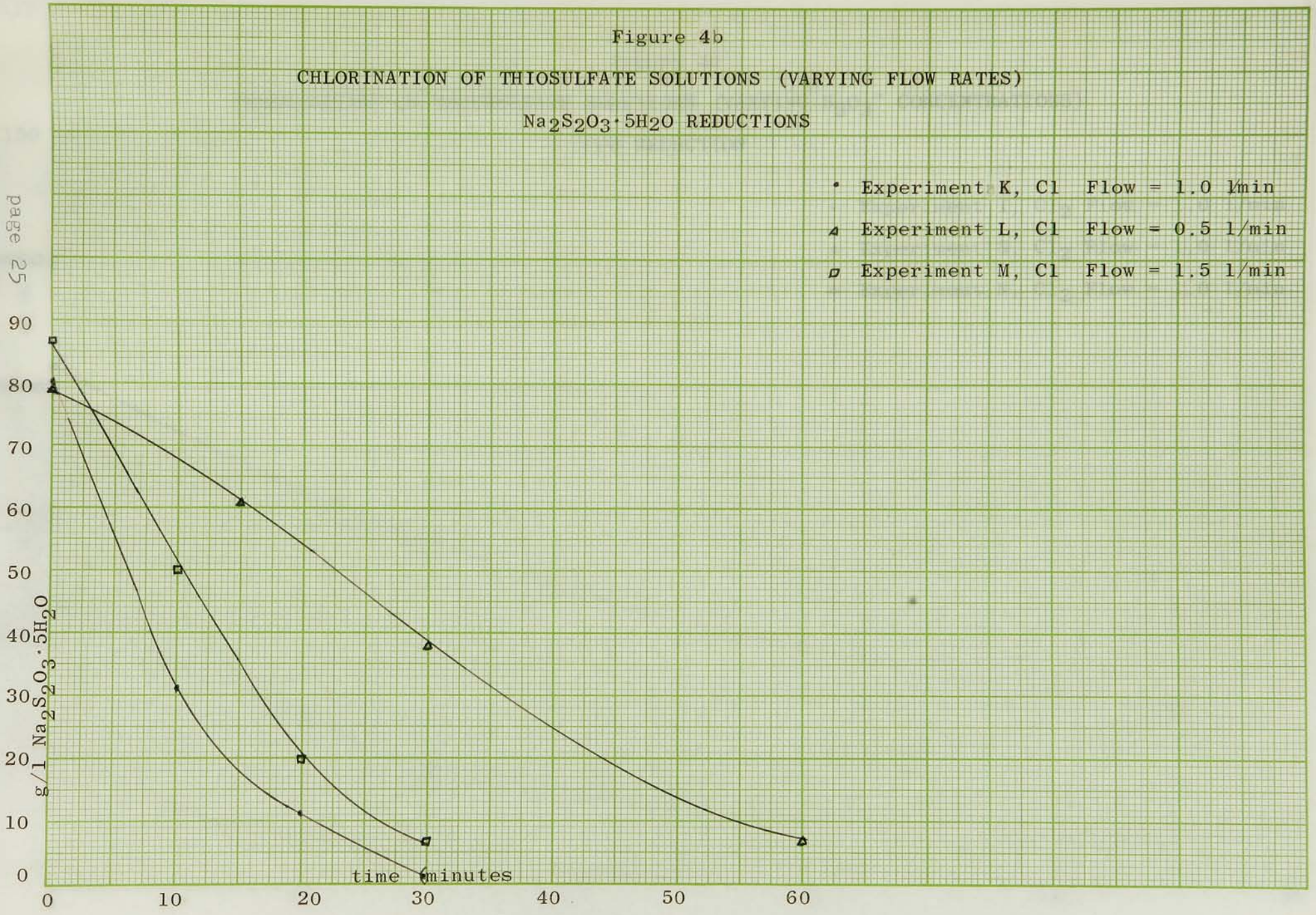


Figure 5a

CHLORINATION OF THIOSULFATE SOLUTIONS (VARYING $S_2O_3^=$ CONCENTRATIONS)

COD REDUCTION

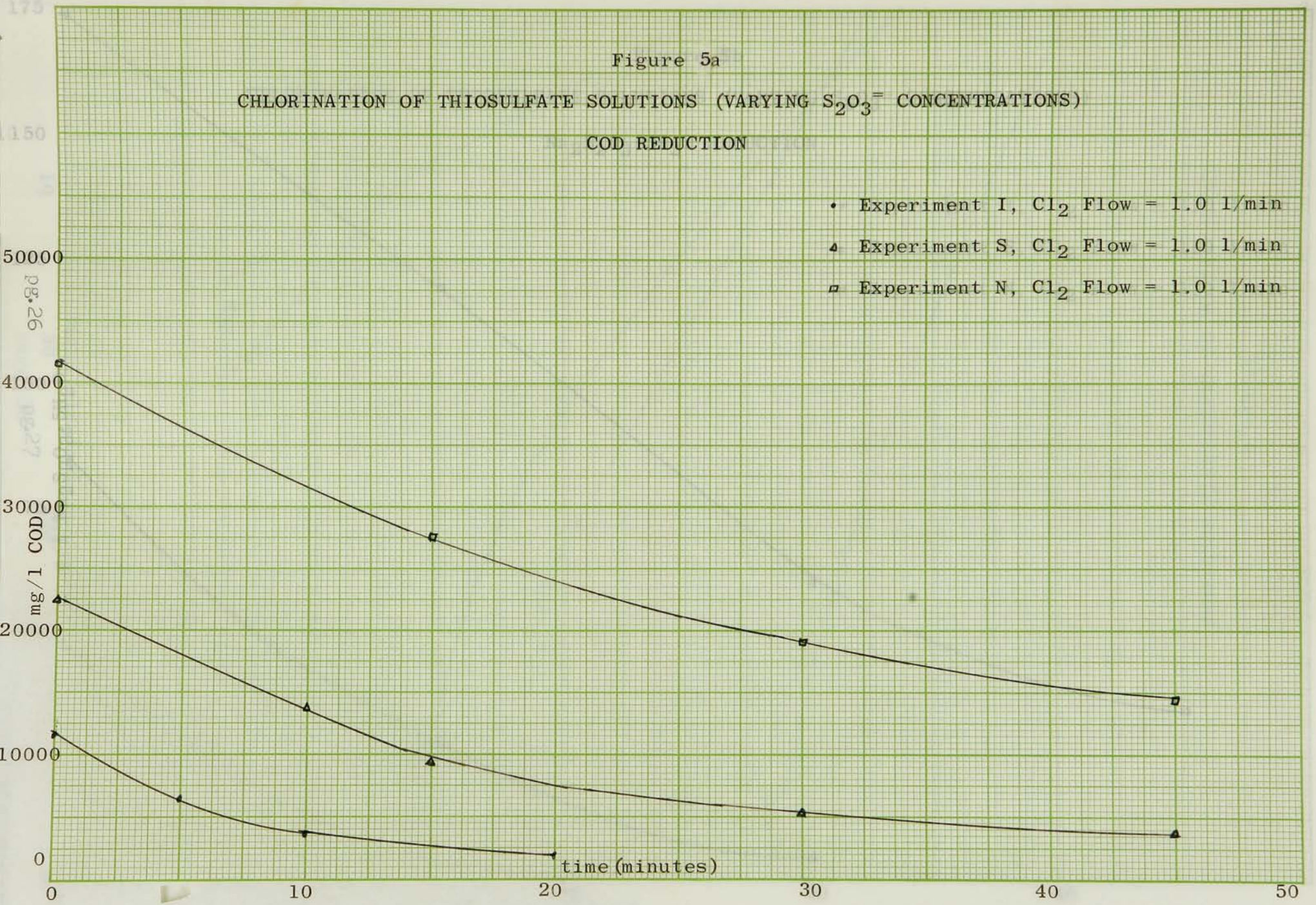


Figure 5b

CHLORINATION OF THIOSULFATE SOLUTIONS (VARYING $S_2O_3^=$ CONCENTRATIONS)

$Na_2S_2O_3 \cdot 5H_2O$ REDUCTION

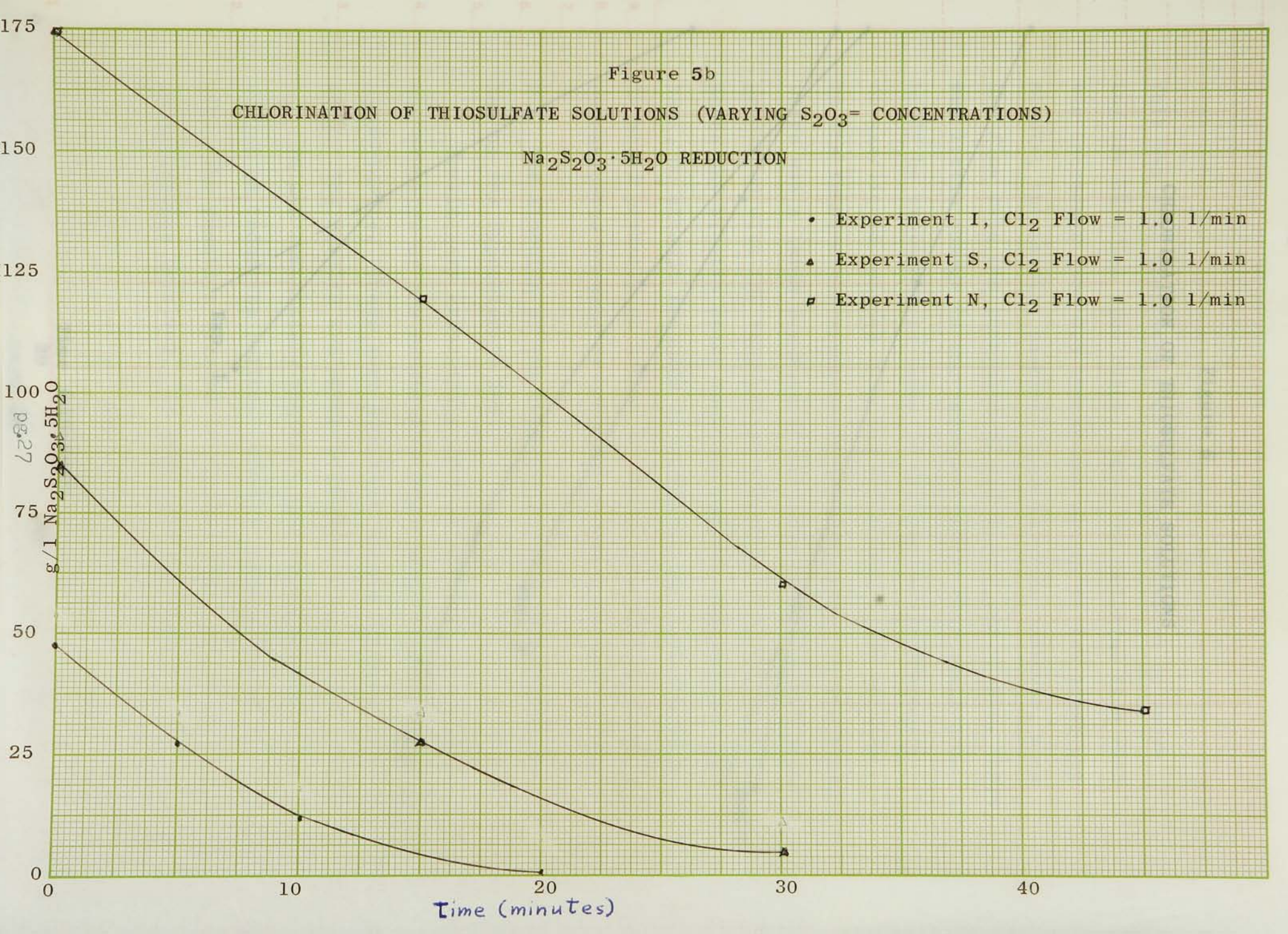
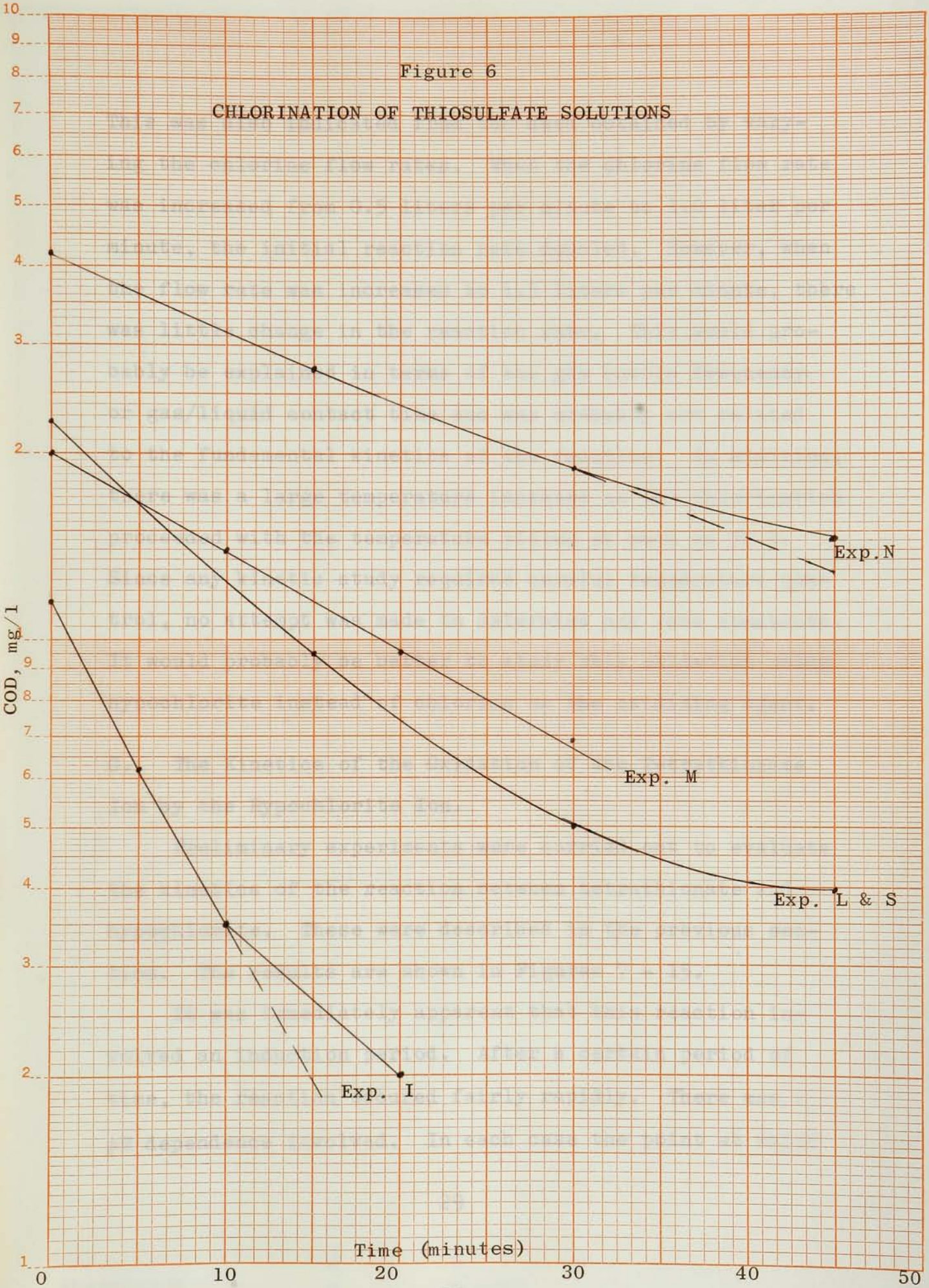


Figure 6

CHLORINATION OF THIOSULFATE SOLUTIONS



This was also indicated from the data obtained by varying the chlorine flow rates. When the chlorine flow rate was increased from 0.5 liters per minute to 1.0 liter per minute, the initial reaction rate doubled. However, when the flow rate was increased to 1.5 liters per minute, there was little change in the reaction rate. This would probably be explained in terms of the gas bubble frequency or gas/liquid contact time and was probably not related to the fundamental kinetics of the reaction. In addition, there was a large temperature increase as the chlorination proceeded with the temperature rising as much as 75 C. Since any kinetic study requires careful temperature control, no attempt was made to determine any rate constants. It would probably be better to study this oxidation using hypochlorite instead of chlorine as the oxidizing agent.

C. The Kinetics of the Oxidation of the Tetrathionate Ion by the Hypochlorite Ion.

Preliminary experiments were carried out to evaluate the kinetics of the reaction between tetrathionate and hypochlorite. These were described in the previous section. The results are shown in Figures 7 - 15.

It was immediately apparent that this reaction involved an induction period. After a certain period of time, the reaction occured fairly rapidly. There was a pH dependence involved. In each case the point at which

Figure 7
2 mm/l Hypochlorite & 2mm/l Tetrathionate

Initial pH = 6.5
Final pH = 2.8

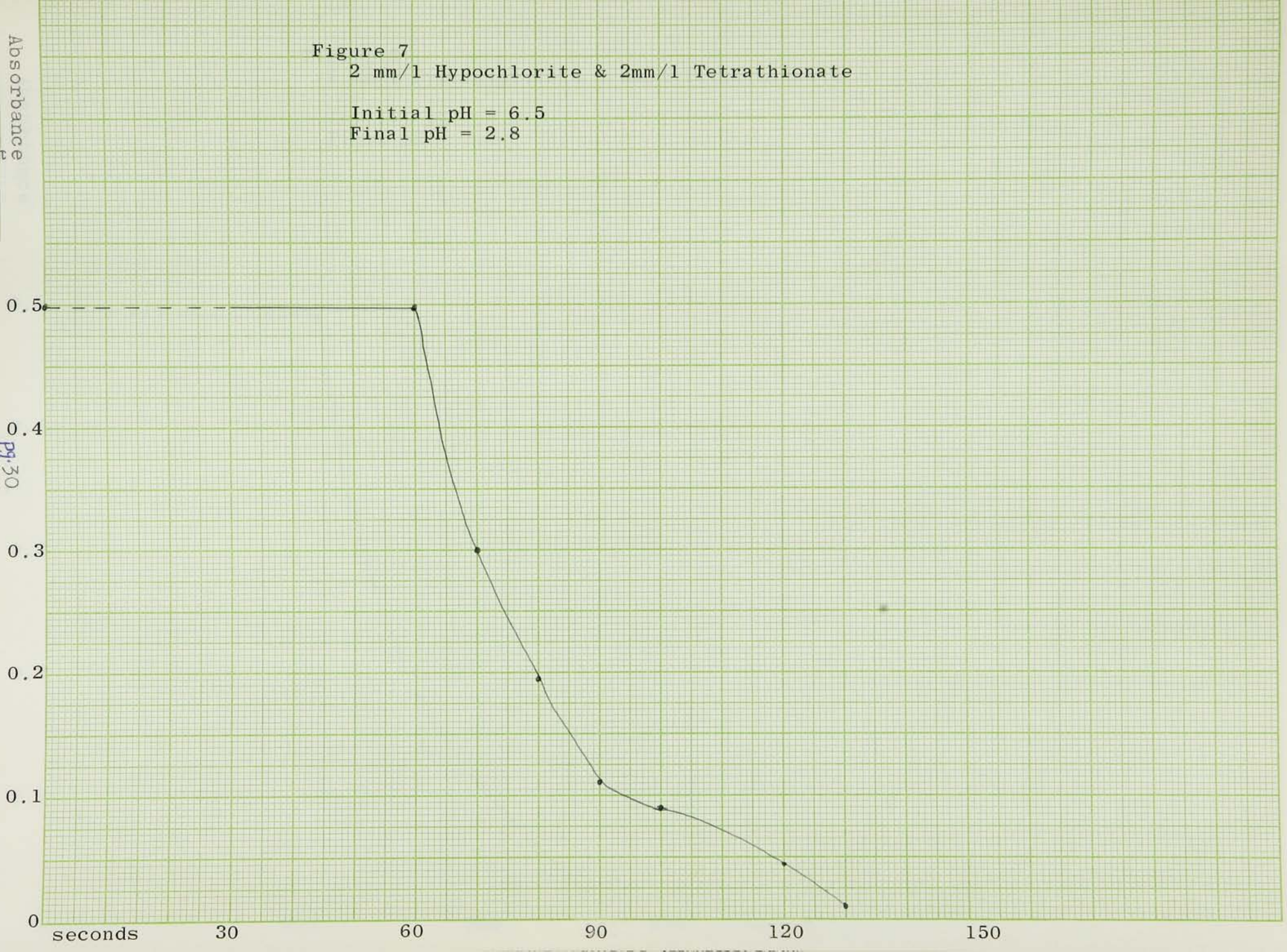


Figure 8
2 mm/l Hypochlorite & 1 mm/l Tetrathionate

Initial pH = 6.8
Final pH = 2.8

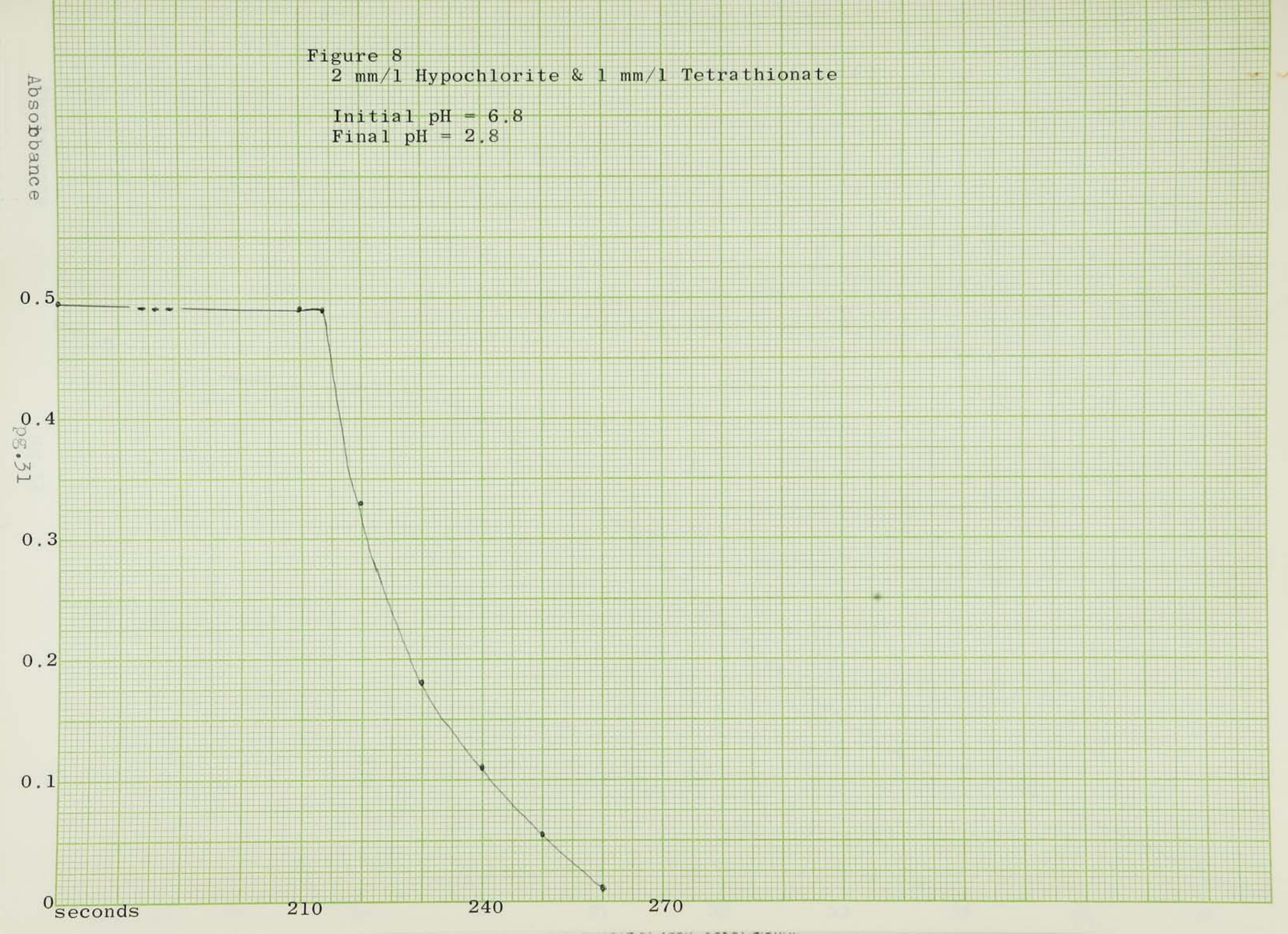


Figure 9
2 mm/l Hypochlorite & 0.5 mm/l Tetrathionate

Initial pH = 7.2
Final pH = 2.8

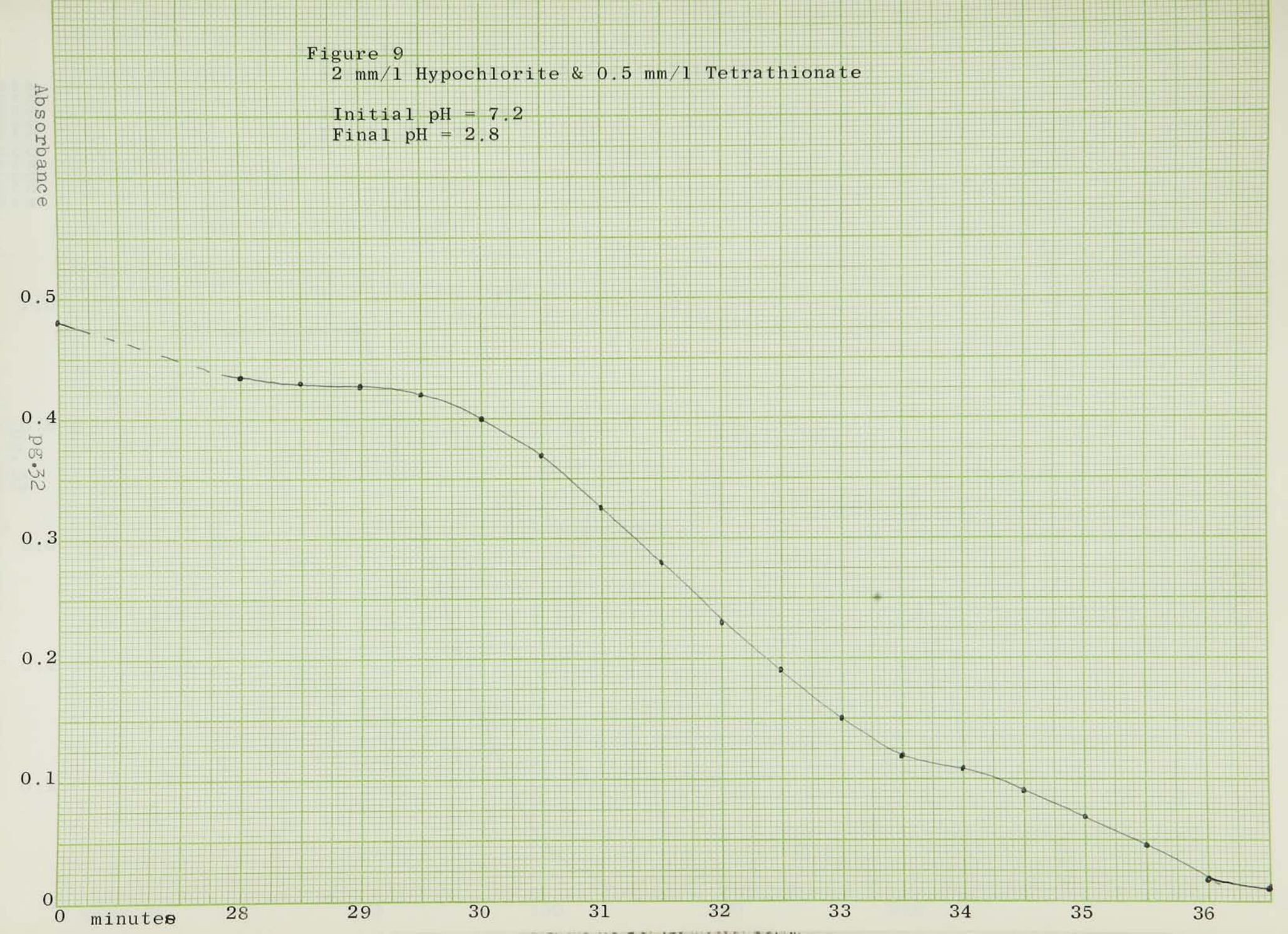


Figure 10
4 mm/l Hypochlorite & 1 mm/l Tetrathionate

Initial pH = 6.8
Final pH = 2.4

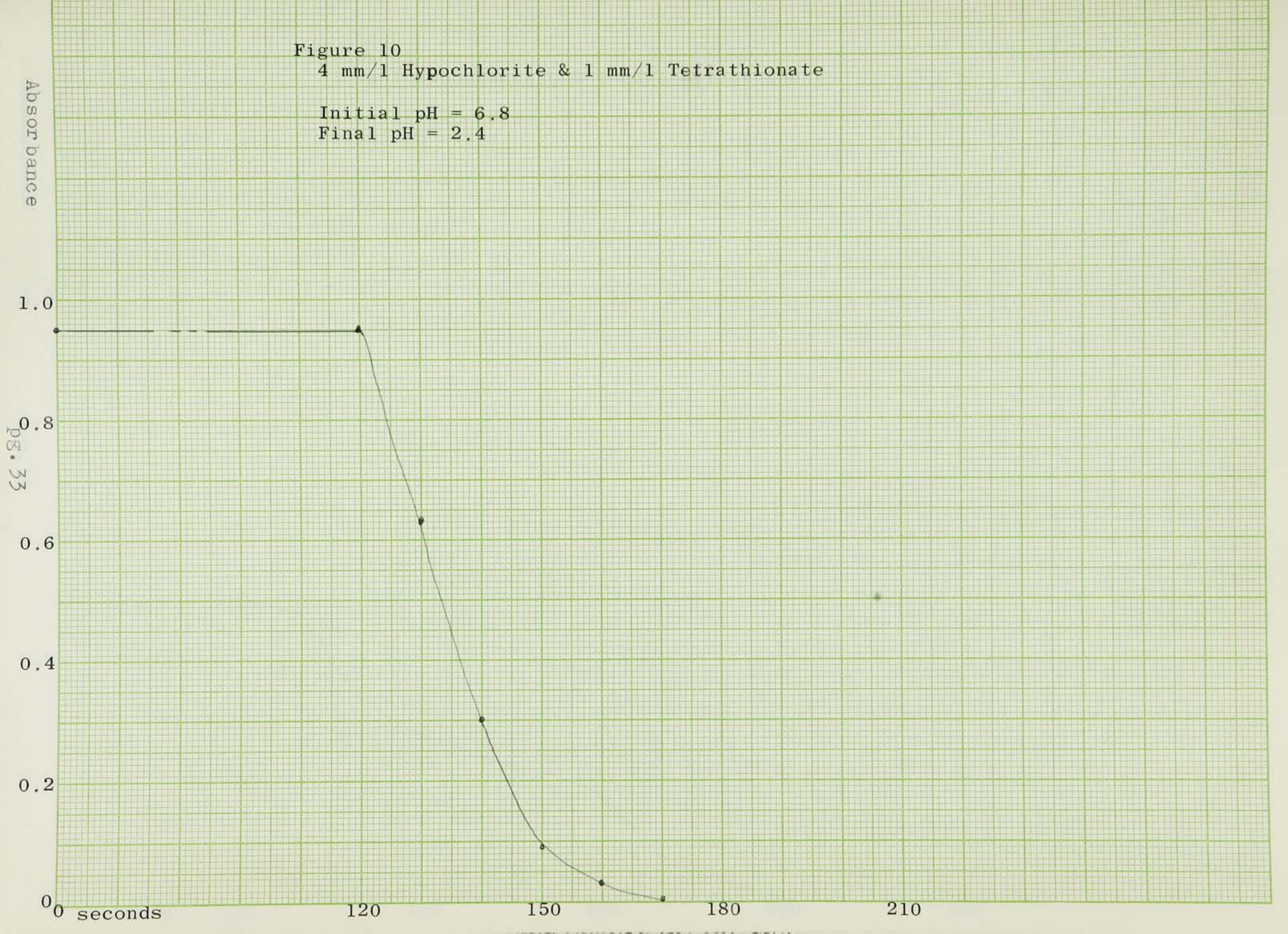


Figure 11
1 mm/l Hypochlorite & 1 mm/l Tetrathionate

Initial pH = 6.8
Final pH = 2.7

pg. 34

Figure 12
2 mm/l Hypochlorite & 1.5 mm/l Tetrathionate

Initial pH = 6.7
Final pH = 2.8

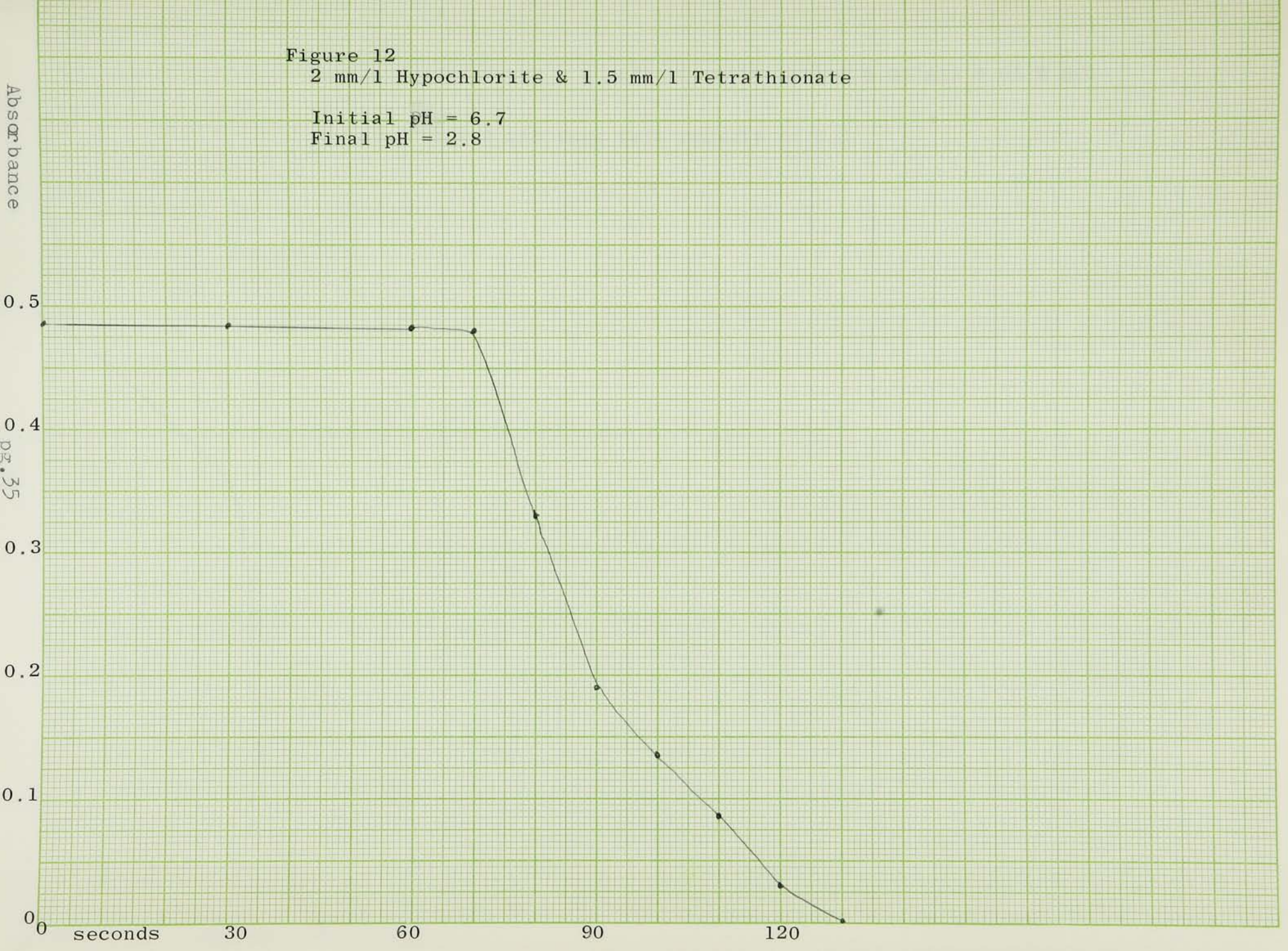


Figure 13
2 mm/l Hypochlorite & 1 mm/l Tetrathionate & 0.05 ml. 0.05 M HCl

Initial pH = 6.8
pH moved to 8.4 and then fell rapidly to 2.8

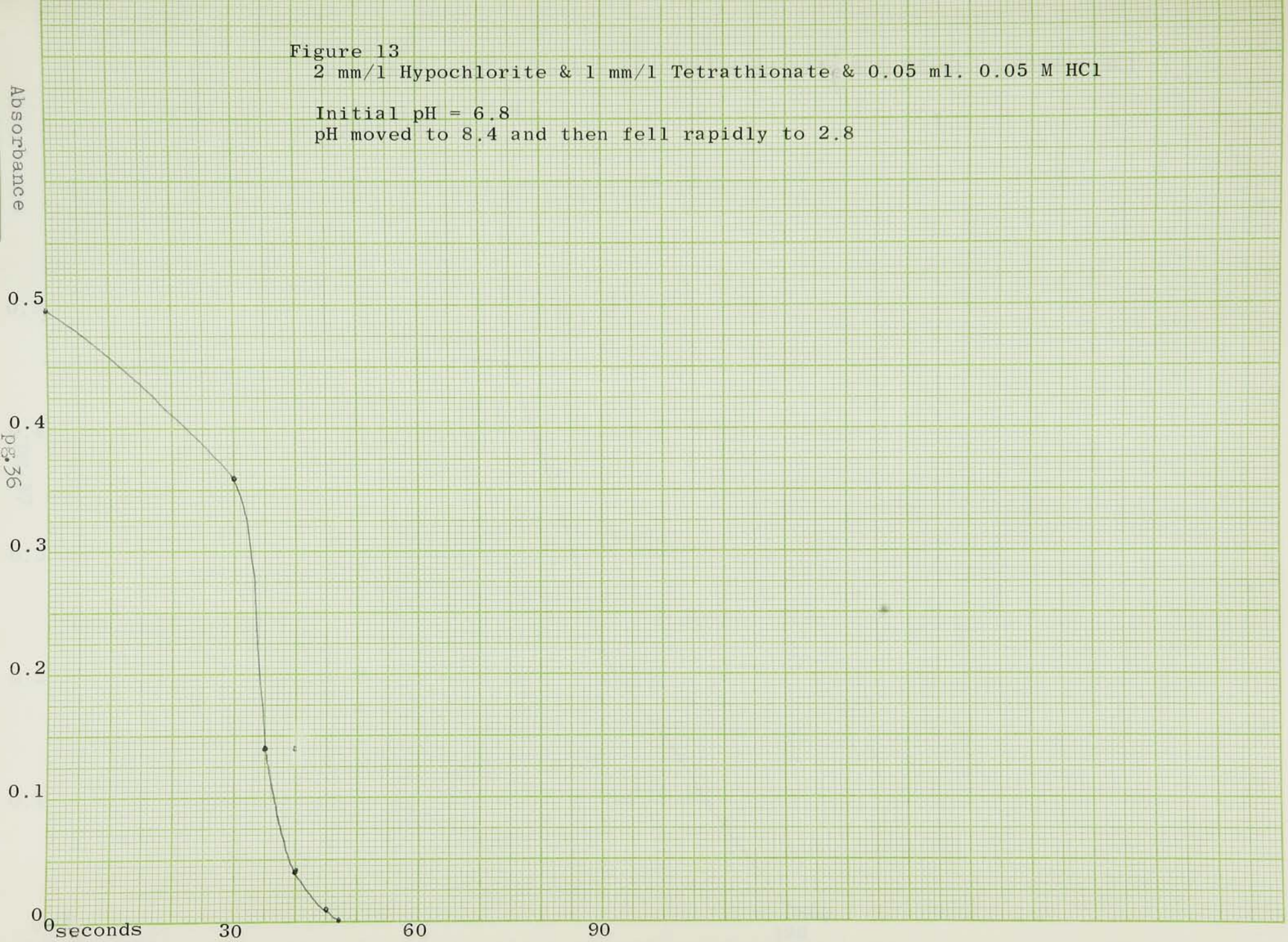


Figure 14
2 mm/l Hypochlorite & 1 mm/l Tetrathionate & 0.05 ml. 0.0125 M HCl

Initial pH = 6.8
Final pH = 2.8

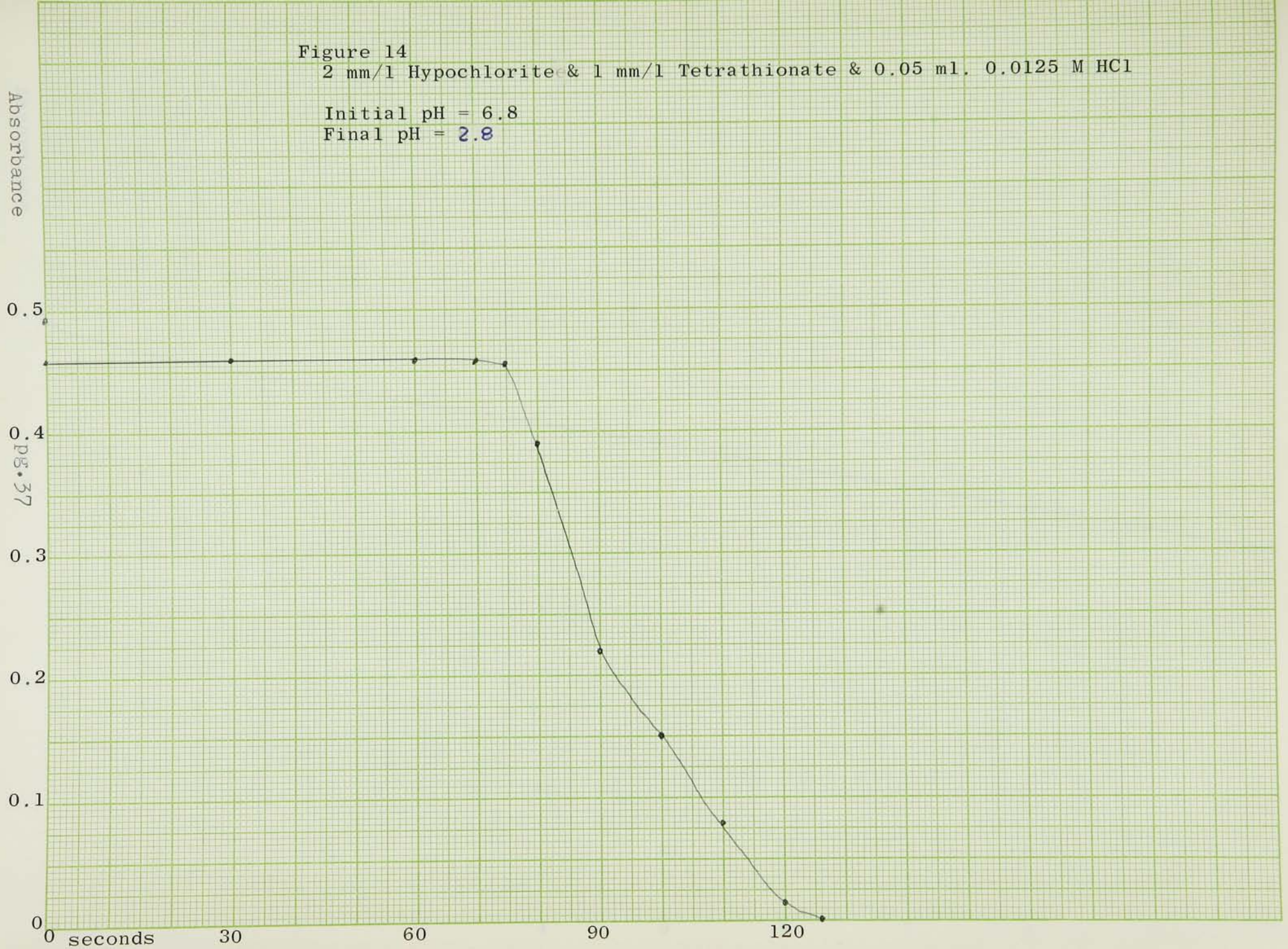
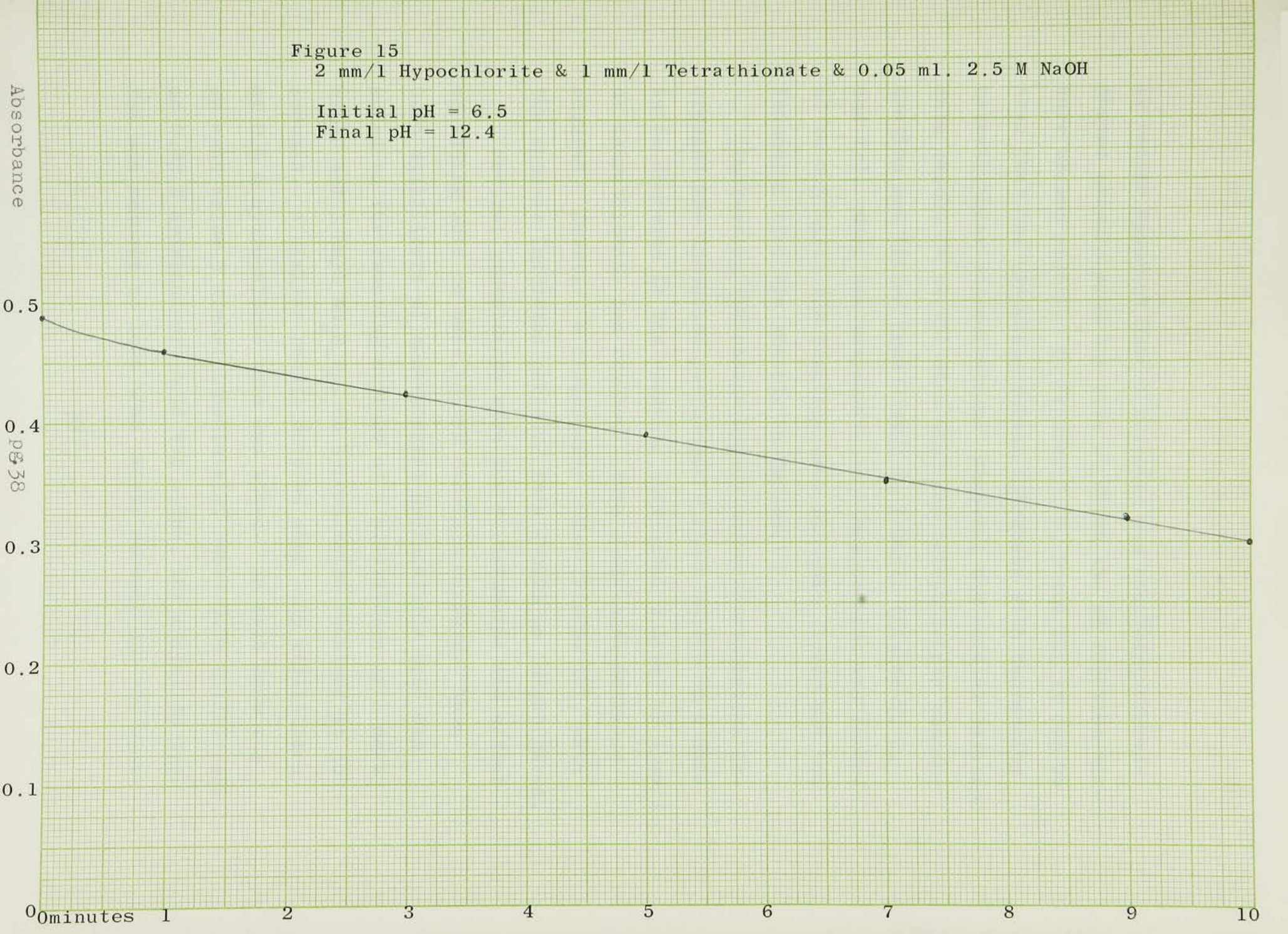


Figure 15
2 mm/l Hypochlorite & 1 mm/l Tetrathionate & 0.05 ml. 2.5 M NaOH

Initial pH = 6.5
Final pH = 12.4



it became apparant that a reaction was occurring corresponded closely with the time at which the pH reaction mixture became acidic. In Figures 7, 8, 9 and 12, it can be seen that the induction period increases with decreasing tetrathionate concentration. However, the initial reaction rate seemed to be the same when the tetrathionate concentration was varied from 2 mm/l to 1 mm/l. (Figure 7, 8, and 12). When the tetrathionate concentration was lowered to 0.5 mm/l, the reaction rate was much slower and the induction time was greatly increased.

Decreasing the sodium hypochlorite concentration increased the induction period but did not result in a definite decrease in the reaction rate until a level of 1 mm/l of tetrathionate was reached. Then a definite decrease occured. However, a discrepancy arose (Figure 11), with the shorter induction period. This should be investigated.

Several experiments were run to determine the effect of adding acid or base to the reacting mixture. When 0.05 milliliters of concentrated hydrochloric acid was added to the reacting mixture of 2 milliliters of 2 mm/l NaClO and 1 mm/l $Na_2S_4O_6$, no hypochlorite remained at 30 seconds. A similar result occured when 0.05 milliliters of 0.6 M hydrochloric acid was added. In each case the pH went below 3 almost immediately. When 0.05 milliliters of 0.05 M hydrochloric acid was added, the induction period was reduced to less than thirty seconds and the rate

was quite fast. This reaction is shown in Figure 13. The pH was initially 8.4 after mixing but quickly went below 3.

In Figure 14, the result of mixing 0.05 milliliters of 0.0125 M hydrochloric acid with the reaction mixture is shown. Here the induction period increased to 75 seconds. Initial pH after mixing was 8.7 and became acidic after a period of about one minute.

Finally, the result of adding 0.05 milliliters of 2.5 M sodium hydroxide to the reaction mixture is shown in Figure 12. In this case the initial pH of the reacting mixture was 12.4 and a much slower reaction occured.

DISCUSSION

It has been shown that the hypochlorination of a thiosulfate solution results in the production of tetrathionate, sulfate, trithionate and probably pentathionate. The latter two probably resulted from secondary reactions involving tetrathionate. It was also shown that the hypochlorination of tetrathionate resulted in the production of trithionate, pentathionate, and sulfate. Again it may be that, with the exception of sulfate, the other species result from secondary reactions. The analytical techniques (Appendix I) are such that it is impossible to detect which species are formed directly. Possibly polarography could be used to establish this.

The study of the kinetics of the chlorination of thiosulfate indicated that this reaction was first order in chlorine and probably pseudo zero order in thiosulfate. This study was not very rigorous.

The study of the kinetics of the hypochlorination of tetrathionate resulted in establishing the existance of a definite induction period which is highly pH dependent. The elucidation of the exact kinetic rate law will require additional work. The rate law will probably involve a hydrogen ion concentration term. In addition, kinetic studies should be done at different temperatures in order to establish the activation energy.

ACKNOWLEDGEMENTS

In conclusion I would like to express my appreciation to Dr. John A. White for his suggestions and criticisms for the improvement of this paper. Finally, I would also like to acknowledge my gratitude to the Eastman Kodak Company for the use of their instruments and chemicals.

BIBLIOGRAPHY

A. SPECIFIC REFERENCES.

1. Cotton and Wilkinson, "Advanced Inorganic Chemistry," 2ed Edition. Interscience Publishers, pg. 550, 1966.
2. Foerster and Hornig, Zeitschrift fur anorganische Chemie, 86, 125, 1922.
3. Voge and Libby, J. Am. Chem. Soc., 59, 2474, 1937.
4. Voge and Libby, J. Am. Chem. Soc., 61, 1032, 1939.
5. Laitinen, H.A., "Chemical Analysis," McGraw Hill Publishers, pg. 400, 1960.
6. Awtrey and Connick, J. Am. Chem. Soc., 73, 1341, 1951.
7. Allen and Keefer, J. Am. Chem. Soc., 77, 2957, 1955.
8. Bradbury and Hanbly, Australian J. Sci. Research,
9. Abel, Z. anorg. u allgem Chem., 74, 395, 1912.
10. Ephraim, F., "Inorganic Chemistry," 6th Edition. Interscience Publishers, pg. 582, 1954.
11. Bushwell and Gallaher, Ind. Eng. Chem, 15, 1187, 1923.
12. Hewett and Mann, J. Chem. Soc., 103, 325, 1913.
13. Lunge, Ber., 12, 404, 1879.
14. Dienert and Wandenbulche, Compt. rend., 167, 29, 1919.
15. Glasstone and Hickling, J. Chem. Soc., 2345 and 2800, 1932.
16. Willson, Anal. Ed., 7, 44, 1935.
17. Cotton and Wilkinson, ibid., pg. 553.
18. Zachariasen, J. Chem. Physics, 2, 109, 1934.
19. Raschig, "Schwefel und Stuckstoffstudies," pg. 284.
20. Weitz and Achterberg, Ber., 61, 399, 1928.
21. Friend, J.N., editor, "A Textbook of Inorganic Chemistry, Vol. VII, Part II," Charles Griffin and Company, London, pg. 198, 1931.
22. Luchow, Zeitschrift fur analytische Chemie, 32, 53, 1893.
23. Cotton and Wilkinson, ibid., pg. 568.
24. Kurtenacher and Goldbach, A. Anorg. Allgen. Chemie., 166, 177-89, 1927.
25. "Standard Methods for the Examination of Water and Wastewater," APHA, 11th Edition, 1960.
26. King, E.L., "How Chemical Reactions Occur," W.A. Benjamin, Inc., 1964, pg. 20.
27. Barrett and Durrant, J. Chem. Soc., 1416, 1927
28. Kurtenacher and Kaufman, Z. Anorg allgem Chem., 148, 43, 1925.

B. GENERAL REFERENCES.

1. Durrant, P.J. and Durrant, B., "Introduction to Advanced Inorganic Chemistry," Longmans, Green and Co., Ltd., 1962.
2. Eisenhauer, H.R., "The Ozonation of Phenolic Wastes," J.W.P.C.F., Vol.40, No.11, Part 1, Nov. 1968, pg. 1887-1899.
3. Gutmann, V., "Halogen Chemistry, Vol.2," Academic Press, New York, 1967.
4. Heslop, R.B. and Robinson, P.L., "Inorganic Chemistry," Elsevier Publishing Company, London, 1960.
5. Kirk, R.E. and Othner, D.F., Editors, "Encyclopedia of Chemical Technology," Vol. 14, The Interscience Encyclopedia, Inc., New York, 1955.
6. Laidler, K.J., "Chemical Kinetics," 2ed Edition, McGraw-Hill Book Company, New York, 1965.
7. Mellor, J.W., "A Comprehensive Treatise On Inorganic and Theoretical Chemistry," Longmans, Green and Co., Ltd., Volume X, London, 1930.
8. "Supplement to Mellor's Comprehensive Treatise On Inorganic and Theoretical Chemistry, Supplement II, Part 1," Longmans, Green and Co., Ltd., London, 1956.
9. Schmidt, M., and Sand, T., J. Inorg. Nucl. Chem., 26, 1165-1171, 1964.

APPENDIX

Outline of the Method for the Determination of Sulfite, Thiosulfate, and Polythionates in the Presence of One Another.[24]

A. $S_2O_3^=$ - Tie up sulfite with formaldehyde and titrate with standard iodine solution.

b. $SO_3^=$ - Use the difference between the iodine titration with and without formaldehyde.

C. Other Polythionates.

1. $S_nO_6^=$ ($n > 3$) + excess $SO_3^= \longrightarrow S_3O_6^= + S_2O_3^=$.
   Tie up excess $SO_3^=$ with formaldehyde and titrate the thiosulfate with iodine.

2. $S_nO_6^=$ ($n > 3$) + CN^- + $H_2O \longrightarrow S_2O_3^= + SO_4^= + SCN^- + HCN$
   Titrate with iodine first to remove sulfite and thiosulfate. Then react with cyanide and titrate the resulting thiosulfate with iodine.

3. $S_nO_6^=$ + excess $S^= \longrightarrow 2\ S_2O_3^= + (n-3)\ S$.
   First titrate with iodine to remove sulfite and thiosulfate. Then remove excess $S^=$ with zinc carbonate. Finally titrate with standard iodine.

4. The trithionate, tetrathionate and pentathionate concentrations can then be calculated.